AFRL-AFOSR-VA-TR-2018-0314

Towards Intrinsically Stretchable Organic Semiconductors

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08/13/2018
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ RTB2
Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 10-07-2018	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* 4/15/2015-4/14/2018
4. TITLE AND SUBTITLE Towards Intrinsically Stretchable Organic Semiconductors		**5a. CONTRACT NUMBER** **5b. GRANT NUMBER** FA9550-15-1-0106 **5c. PROGRAM ELEMENT NUMBER**
6. AUTHOR(S) Zhenan Bao		**5d. PROJECT NUMBER** **5e. TASK NUMBER** **5f. WORK UNIT NUMBER**
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Stanford University Department of Chemical Engineering Stanford, CA 94305		**8. PERFORMING ORGANIZATION REPORT NUMBER**
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)		**10. SPONSOR/MONITOR'S ACRONYM(S)** **11. SPONSOR/MONITOR'S REPORT NUMBER(S)**

12. DISTRIBUTION / AVAILABILITY STATEMENT

Distribution A: approved for public release

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report summarizes results supported by grant no. FA9550-15-1-0106. We report: 1. Development of stretchable semiconductors 2. Understanding of stretchable dielectric materials; 3. Development of stretchable conductors; 4. Fabrication of stretchable organic transistors.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Award Title: Towards Intrinsically Stretchable Organic Semiconductors

The aim of this AFOSR-sponsored project was to understand the molecular design concepts towards intrinsically stretchable semiconductors. Towards this aim, we have successfully developed basic understanding of structure-property relationships, achieved new design concepts by incorporating dynamic bonds as conjugation breaker for the first time into conjugated polymers and by exploring soft crosslinkers. In addition, we also developed new understandings on stretchable conducting polymer design and stretchable and self-healable dielectric design. These work together significantly advanced our understanding of molecular design for essential electronic materials needed for fabrication of stretchable electronic devices. Below, we provide summaries for significant findings in each topic:

(i) Demonstration of intrinsically stretchable and heablable polymer semiconductors by incorporation of dynamic bonds as conjugation breaker

The results from this work have been published in:
J. Y. Oh, S. Rondeau-Gagné, Y.-C. Chiu, A. Chortos, F. Lissel, G.-J. N. Wang, B. C. Schroeder, T. Kurosawa, J. Lopez, T. Katsumata, J. Xu, C. Zhu, X. Gu, W.-G. Bae, Y. Kim, L. Jin, J. W. Chung, J. B.-H. Tok, Z. Bao, "Intrinsically stretchable and healable semiconducting polymer for organic transistors", **Nature**, 539, 411-415, 2016.

The key findings from the paper are:
We demonstrated a new design concept for stretchable semiconducting polymers, which involves introducing chemical moieties to promote dynamic non-covalent crosslinking of the conjugated polymers. These non-covalent crosslinking moieties are able to undergo an energy dissipation mechanism through breakage of bonds when strain is applied, while retaining high charge transport abilities. As a result, our polymer is able to recover its high field-effect mobility performance (more than 1 cm^2/Vs) even after a hundred cycles at 100 per cent applied strain. Organic thin-film field-effect transistors fabricated from these materials exhibited mobility as high as 1.3 cm^2/Vs and a high on/off current ratio exceeding a million. The field-effect mobility remained as high as 1.12 cm^2/Vs at 100 per cent strain along the direction perpendicular to the strain. The field-effect mobility of damaged devices can be almost fully recovered after a solvent and thermal healing treatment. Finally, we successfully fabricated a skin-inspired stretchable organic transistor operating under deformations that might be expected in a wearable device.

(ii) Demonstration of soft crosslinking strategy for improved fracture resistance

The results from this work have been published in:
G.-J. N. Wang, L. Shaw, J. Xu, T. Kurosawa, B. C. Schroeder, J. Y. Oh, S. J. Benight, Z. Bao, "Inducing elasticity through oligo-siloxane crosslinks for intrinsically stretchable semiconducting polymers", **Adv. Func. Mater.**, 26, 7254-7262, 2016.

The key findings from the paper are:
In approach one, we propose soft crosslinking as a strategy to improve fracture as well as fatigue resistance of a semiconductive polymer. Diketopyrrolopyrrole (DPP) based polymers are crosslinked with soft siloxane oligomers to give a stretchable films stable up to 150% and could undergo 500 cycles of 100% strain without signs of nano-cracks. Organic field-effect transistors were prepared to assess the electrical properties of the crosslinked film under cyclic loading. A steady μ^{avg} of 0.4 cm^2/Vs was obtained in the perpendicular to strain direction after 500 cycles of 20% strain. The μ^{avg} in the parallel to strain direction was however compromised due to the formation of wrinkles. This work sheds light onto the importance of developing elastic materials for stretchable electronics and wrinkling as a failure mechanism from fatigue.

(iii) Understanding elastic dielectric material selection

The results from this work have been published in:

D. Kong, R. Pfattner, A. Chortos, C. Lu, A. C. Hinckley, C. Wang, W.-Y. Lee, J. W. Chung, Z. Bao, "Capacitance Characterization of Elastomeric Dielectrics for Applications in Intrinsically Stretchable Thin Film Transistors", **Adv. Func. Mater**., 26, 4680-4686, 2016. ***and***

C. Wang and W.-Y. Lee and D. Kong and R. Pfattner, G. Schweicher, R. Nakajima, C. Lu, J. Mei, T. H. Lee, H.-C. Wu, J. Lopez, Y. Diao, X. Gu, S. Himmelberger, W. Niu, J. R. Matthews, M. He, A. Salleo, Y. Nishi, Z. Bao, "Significance of the double-layer capacitor effect in polar rubbery dielectrics and exceptionally stable low-voltage high transconductance organic transistors", Sci. Rep., 5, 17849, 2015.

The key findings from these papers are:
Stretchable electronics exhibit unique mechanical properties to expand the applications areas of conventional electronics based on rigid wafers. Intrinsically stretchable thin film transistor is an essential component for functional stretchable electronics, which presents a great opportunity to develop mechanically compliant electronic materials. Certain elastomers have been recently adopted as the gate dielectrics, but their dielectric properties have not been thoroughly investigated for such applications. Here, a charging measurement technique with a resistor–capacitor circuit is proposed to quantify the capacitance of the dielectric layers based on elastomers. As compared with conventional methods, the technique serves as a universal approach to extract the capacitance of various elastomers under static conditions, irrespective of the charging mechanisms. This technique also offers a facile approach to reliably quantify the mobility of thin film transistors based on elastomeric dielectrics, paving the way to utilize this class of dielectrics in the development of intrinsically stretchable transistors.

We observed a significant double-layer capacitance effect in polar rubbery dielectrics, even when present in a very low ion concentration and conductivity. We observed that this effect can greatly enhance the OFET transconductance when driven at low voltages. Specifically, when the polar elastomer poly(vinylidene fluoride-cohexafluoropropylene) (e-PVDF-HFP) was used as the dielectric layer, despite a thickness of several micrometers, we obtained a transconductance per channel width 30 times higher than that measured for the same organic semiconductors fabricated on a semicrystalline PVDF-HFP with a similar thickness. After a series of detailed experimental investigations, we attribute the above observation to the double-layer capacitance effect, even though the ionic conductivity is as low as 10–10 S/cm. Different from previously reported OFETs with double-layer capacitance effects, our devices showed unprecedented high bias-stress stability in air and even in water.

(iv) Stretchable and self-healable dielectrics based on metal-ligand coordination:

The results from this work have been published in:
Y.-L. Rao, A. Chortos, R. Pfattner, F. Lissel, Y.-C. Chiu, V. Feig, J. Xu, T. Kurosawa, X. Gu, C. Wang, M. He, J. W. Chung, Z. Bao, "Stretchable Self-healing Polymeric Dielectrics Crosslinked Through Metal-Ligand Coordination", **J. Amer. Chem. Soc.**, 138, 6020–6027, 2016 *and*

C. Wang and C.-H. Li, C. Wang, C. Keplinger, J.-L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.-Z. You, Z. Bao, "A Highly Stretchable Autonomous Self-Healing Elastomer", **Nature Chemistry**, 8, 618–624, 2016.

The key findings from the paper are:
It is a challenge to synthesize materials that possess the properties of biological muscles strong, elastic and capable of self-healing. Herein we report a network of poly(dimethylsiloxane) polymer chains crosslinked by coordination complexes that combines high stretchability, high dielectric strength, autonomous self-healing and mechanical actuation. The healing process can take place at a temperature as low as −20 °C and is not significantly affected by surface ageing and moisture. The crosslinking complexes used consist of 2,6-pyridinedicarboxamide ligands that coordinate to Fe(III) centres through three different interactions: a strong pyridyl–iron one, and two weaker carboxamido–iron ones through both the nitrogen and oxygen atoms of the carboxamide groups. As a result, the iron–ligand bonds can readily break and re-form while the iron centres still remain attached to the ligands through the stronger interaction with the pyridyl ring, which enables reversible unfolding and refolding of the chains. We hypothesize that this behavior supports the high stretchability and self-healing capability of the material.

A self-healing dielectric elastomer is achieved by the incorporation of metal− ligand coordination as cross-linking sites in nonpolar polydimethylsiloxane (PDMS) polymers. The ligand is 2,2′ -bipyridine-5,5′ -dicarboxylic amide, while the metal salts investigated here are Fe^{2+} and Zn^{2+} with various counter-anions. The kinetically labile coordination between Zn^{2+} and bipyridine endows the polymer fast self-healing ability at ambient condition. When integrated into organic field-effect transistors (OFETs) as gate dielectrics, transistors with $FeCl_2$ and $ZnCl_2$ salts cross-linked PDMS exhibited increased dielectric constants compared to PDMS and demonstrated hysteresis-free transfer characteristics, owing to the low ion conductivity in PDMS and the strong columbic interaction between metal cations and the small Cl^- anions which can prevent mobile anions drifting under gate bias. Fully stretchable transistors with $FeCl_2$ -PDMS dielectrics were fabricated and exhibited ideal transfer characteristics. The gate leakage current remained low even after 1000 cycles at 100% strain. The mechanical robustness and stable electrical performance proved its suitability for applications in stretchable electronics. On the other hand, transistors with gate dielectrics containing large-sized anions (BF_4^-, ClO_4^-, CF_3^-, SO_3^-) displayed prominent hysteresis due to mobile anions drifting under gate bias voltage. This work provides insights on future design of self-healing stretchable dielectric materials based on metal− ligand cross-linked polymers.

Publications Acknowledging Support by AFOSR Grant FA9550-15-1-0106 (18 published)

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2. J. Y. Oh, S. Rondeau-Gagné, Y.-C. Chiu, A. Chortos, F. Lissel, G.-J. N. Wang, B. C. Schroeder, T. Kurosawa, J. Lopez, T. Katsumata, J. Xu, C. Zhu, X. Gu, W.-G. Bae, Y. Kim, L. Jin, J. W. Chung, J. B.-H. Tok, Z. Bao, "Intrinsically stretchable and healable semiconducting polymer for organic transistors", **Nature**, 539, 411-415, 2016.
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6. J.-C. Lai, J.-F. Mei, X.-Y. Jia, C.-H. Li, X.-Z. You, Z. Bao, "A Stiff and Healable Polymer Based on Dynamic-Covalent Boroxine Bonds", **Adv. Mater.,** 28, 8277-8282, 2016.

7. C.-H. Li, C. Wang, C. Keplinger, J.-L. Zuo, L. Jin, Y. Sun, P. Zheng, Y. Cao, F. Lissel, C. Linder, X.-Z. You, Z. Bao, "A Highly Stretchable Autonomous Self-Healing Elastomer", **Nature Chemistry**, 8, 618–624, 2016.

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<u>Stretchable Conductors:</u>

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17. A. Chortos and J. Liu, Z. Bao, Pursuing Prosthetic Electronic Skin", **Nature Materials**, 15, 937-950, 2016.
18. G.-J. N. Wang, A. Gasperini, Z. Bao, "Stretchable Polymer Semiconductors for Plastic Electronics", **Adv. Electron. Mater.,** 4, 2, 1700429, 2018.

Patent applications:

Docket #	Docket Inventor List	Country	Patent Type	Patent Status	Serial #	Filing Date
S14-192	Zhenan Bao, Cheng-Hui Li, and Chao Wang	USA	Provisional	Expired	62/101,763	1/9/2015
		USA	Provisional	Expired	62/270,841	12/22/2015
		USA	Original	Pending	15/385,674	12/20/2016

AFOSR Deliverables Submission Survey

Response ID:10178 Data

1.

Report Type

Final Report

Primary Contact Email
Contact email if there is a problem with the report.

zbao@stanford.edu

Primary Contact Phone Number
Contact phone number if there is a problem with the report

6507232419

Organization / Institution name

Stanford University

Grant/Contract Title
The full title of the funded effort.

Towards Intrinsically Stretchable Organic Semiconductors

Grant/Contract Number
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-15-1-0106

Principal Investigator Name
The full name of the principal investigator on the grant or contract.

Zhenan Bao

Program Officer
The AFOSR Program Officer currently assigned to the award

Kenneth Caster

Reporting Period Start Date

04/15/2015

Reporting Period End Date

04/14/2018

Abstract

This report summarizes results supported by grant no. FA9550-15-1-0106. We report: 1. Development of stretchable semiconductors 2. Understanding of stretchable dielectric materials; 3.

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US patent serial no. 15/385/674 filed on Dec. 20, 2016

Do you plan to pursue a claim for personal or organizational intellectual property?

Yes

Changes in research objectives (if any):

No

Change in AFOSR Program Officer, if any:

From Dr. Charles Lee to Dr. Kenneth Castner

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
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